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Controlled Functionalization of Olefin/styrene Copolymers through Free Radical Processes

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ABSTRACT

The functionalization of styrene-b-(ethylene-co-1-butene)-b-styrene triblock copolymer (SEBS) and styrene-co-butadiene (SBR) random copolymer by free radical processes is presented. SEBS was functionalized in the melt with diethyl maleate (DEM) and dicumyl peroxide (DCP) as initiator. The functionalization degree (FD) ranges from 0.1 to 1.6% mol and depends on the feed composition and in particular on the DEM/DCP ratio. Such functionalization takes place with a very large preference at the aliphatic carbons of the polyolefin block.

The functionalization of SBR was performed by radical addition in solution of two functional thiols (thioglicolic acid and its aliphatic ester), in the presence of free radical initiators. The addition occurs at the vinyl double bonds of the 1–2 butadiene units with high selectivity. FD can be tuned in the range 1–10 mol%. These data are rationalized in the frame of the general reaction mechanism of free radical polymerization. A general reaction scheme is proposed which allows the design of proper conditions for favoring functionalization versus degradation and crosslinking depending on the nature of molecules and macromolecules involved. *Copyright © 2000 John Wiley & Sons, Ltd.*

KEYWORDS: SEBS copolymer; SBR copolymer; functionalization; radical additions; thiols

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INTRODUCTION

Free radical processes are widely used in organic and polymer chemistry thanks to their ease of use and economic feasibility, their selectivity being, however, generally poor. Significant advances have been obtained in recent years as far as controlled free radical polymerization is concerned. Narrower molecular weight distribution, increase of molecular weight with conversion and block copolymer structures have been reported when metal assisted or stabilized radical initiators were used [1, 2]. Much less has been done as far as controlled functionalization of polyolefins through free radical processes is concerned. The problem is really complex owing to the reaction conditions, the heterogeneity of the system and the high temperature needed to eliminate any crystallinity and to have good reological properties. A few studies have been reported in the literature about the determination of the molecular structure of the functional groups inserted into the polyolefin chain; in particular these studies could demonstrate that oligomeric branching can be formed with maleic anhydride (MAH) [3], while substantially monomeric side chains are formed with diethylmaleate (DEM) [4]. In previous papers we reported detailed results showing how selection of operating parameters, without altering the conventional functional process, could provide a partial control of the functionalization of ethylene polymers in the melt when DEM and dicumylperoxide (DCP) were used as reagents [5]. Indeed disproportionation (degradation) and recombination (chain extension to crosslinking) of the macromol-

ecular radical is inhibited by prompt reaction with the monomer, while transfer takes place at higher rate than monomer propagation. Proper selection of coreagents (DEM and DCP) as well as of their concentration in respect to the polymer allowed a mathematical model to be developed describing the process on the basis of the grafting reaction only [5]. Even for the structurally simple polyolefins, a different reactivity was generally observed by changing the number of side chains from high-density polyethylene (HDPE) to various linear low-density polyethylenes (LLDPEs), ethylene propylene copolymer (EPR) and polypropylene (PP). The degradation increased and the chain extension decreased in that order, while the functionalization degree (FD) was the highest for intermediate highly branched ethylene/1-olefins copolymers (LLDPE and EPR) [6]. An even more dramatic effect was observed in case of ethylene propylene dieme monomer (EPDM), where the presence of double bonds was responsible for increased crosslinking, because of allylic protons, and functionalization, thanks to the occurrence of the ene reaction [5, 7].

Styrene copolymers with diolefins [styrene-co-butadiene, random (SBR), and block (SBS)] or 1-alkenes (styrene-6-(ethylene-co-1-butene)-6-styrene, SEBS) deserve similar industrial interest in the field of elastomers and themoplastic elastomers and have been subjected to studies aimed at introducing functional groups, allowing a better interaction particularly with other polymers and inorganic fillers [8–12]. In the case of SEBS the very limited amount of aliphatic double bonds allowed the same systems developed for aliphatic polyolefins to be applied. In contrast, the massive presence of double bonds in SBR or SBS commands a different approach and in particular a much-improved transfer capacity by the functionalizing molecule. The present paper is therefore devoted to describe the partially controlled introduction of carboxylate groups in the above styrene-containing macromolecules based on radical processes in which initiation and transfer dominate over propagation and termination.

EXPERIMENTAL

Materials

The block copolymer SEBS Europrene Sol TH 212 was supplied by Enichem Elastomeri and was employed without further purification. This polymer contains 19% by mol of styrene units and 32.4% of 1,2-butadiene, 48.6% of 1,4-butadiene units; $\overline{M}_w = 65–70 \times 10^3$ and $\overline{M}_w/\overline{M}_n = 1.03–1.11$. Atactic polystyrene (PS) with $\overline{M}_n = 50 \times 10^3$ and $\overline{M}_w/\overline{M}_n = 2.5$ was supplied by Repsol and used without purification. Linear LLDPE was supplied by Enichem and was an ethylene 1-butene copolymer containing 14% by mol of 1-butene units.

SBR copolymer, kindly provided by EniChem SpA (Ravenna), contained 27 wt% of styrene (16 mol%), 73 wt% of butadiene (1,4 units about 47% mol and vinyl units of about 37 mol%) and had average viscosimetric molecular weight around 330,000.

Diethylmaleate (DEM, Aldrich) was purified by distillation. Dicumyl peroxide (DCP, Aldrich), thioglycolic acid (TGA) (Carlo Erba), ethyl mercaptoacetate (EMA) (Aldrich Chemical Co.) and, benzoyl peroxide (BPO) (Aldrich Chemical Co.) were used without further purification. α,α′-Azobisisobutyronitrile (AIBN) (Carlo Erba) was purified by recrystallization from ethanol. The used solvents were purified by standard procedures.

Characterization

Infrared spectra were performed with a 'Perkin Elmer FT-IR 1750' Fourier transform spectrometer; on films cast from a chloroform solution on a KBr window; or by deposition of a drop of liquid between two KBr windows.

Proton magnetic resonance spectra were performed with a 'Varian Gemini 200 MHz' spectrometer; all the spectra were made in solution of deutero-chloroform, chemical shifts were assigned in ppm using tetramethylsilane (TMS) as internal standard.

Differential scanning calorimetry analysis was performed with a 'Perkin Elmer DSC7' calorimeter equipped with CCA7 for temperature control in the temperature range −90 °C to +30 °C at the scanning rate of 20 °C/min. The calibration was been carried out using mercury (m.p. −38.4 °C) and Indium (m.p. 156.2 °C) standards.

The solid-state nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AMX-300 WB spectrometer, equipped with a 4 mm cross-polarization-magic angle spinning (CP/MAS) probe, at the operating frequency of 75.47 MHz for ^{13}C.

Functionalization Reaction

Functionalization of SEBS was performed in a Brabender mixer (Plastograph) at 220 °C operating under a nitrogen atmosphere as described elsewhere [13,14]. The functionalization reaction of a mixture of LLDPE and atactic PS was performed using the same procedure, and the reaction products were dissolved in toluene and then precipitated by acetone addition. In this way it was possible to separate PS and LLDPE after functionalization.

SBR was dissolved in pure toluene under nitrogen and thiols were added up to 25 mol% of thiol with respect to the total moles of monomeric units of the copolymer. AIBN or DCP was then added and the mixture heated to 90 °C for 2.5 hr according to the previously described procedure [15].

Processing in a Brabender Mixer

SEBS, SBS, SBR, PS and polybutadiene (PB) were treated in a Brabender mixer at variable high temperature for several minutes as such or in the presence of free radical initiator (DCP or AIBN, 0.5 or 0.1% wt).

The residual polymer was extracted with boiling chloroform. The results are reported in Table 1.

TABLE 1. Variation of Solubility of Olefins and Styrene Polymers Determined by Thermal and Free Radical Initiated Degradation and Chain Extension

Polymer	*T (°C)*	*Duration (min)*	*Thermal Sol. (% wt)*	*Free radical*	
				Initiator (% wt)	*Sol. (% wt)*
HDPE	200	30	100[a]	DCP 1.5	40[a]
LLDPE	200	30	100[a]	DCP 1.0	62[a]
EPR	190	30	100[a]	DCP 1.0	88[a]
iPP	190	30	85[a]	DCP 0.5	96[a]
SEBS	220	16	100[b]	DCP 0.5	100[b]
EPDM	190	30	100[a]	DCP 1.0	1[a]
SBS	180	9	98[b]	DCP 0.5	23[b]
SBR	60	150	100[b]	AIBN 0.1	0[b]
PS	190	25	100[b]	DCP 0.1	100[b]
PB	180	9	100[b]	DCP 0.1	34[b]

[a] Toluene as solvent.
[b] $CHCl_3$ as solvent.

RESULTS AND DISCUSSION

Processing in a Brabender Mixer

Before performing the functionalization reaction, the thermal and free radical reactivity of SEBS and SBR was evaluated under the same temperature and duration conditions successively used for grafting the functional molecules. For comparison analogous experiments were carried out with atactic PS and a random copolymer of 1,4 (90 mol%) and 1,2 (10 mol%) butadiene units obtained by anionic polymerization. As shown in the data reported in Table 1, SEBS does not undergo any gel formation even in the presence of 0.5 wt% DCP; the same behavior is observed for PS, while saturated polyolefins (LLDPE) give a certain degree of crosslinking. SBS (SEBS precursor), which contains double bonds in the butadiene blocks, gives under the same conditions some gel formation to an extent appreciably lower than PB. SBR at lower temperature but longer duration gives extensive crosslinking with AIBN. These data indicate that the presence of styrene units markedly reduces the chain extension by recombination of macroradicals. Indeed no gel formation is observed unless double bonds are present. Even in this last case, however, the chain extension seems to be appreciably hindered.

Grafting of Diethylmaleate onto Styrene/1-alkenes Block Copolymers (SEBS)

The same approach could be used for SEBS as for ethylene polymers by using DEM as functionalizing monomer and DCP as radical initiator with possible differences in process temperature connected to the different thermal characteristic of the styrene-containing polymers. Experiments with polystyrene, working at 190 °C, and also with DEM and DCP, have indicated a lower tendency to functionalization of this polymer with respect to polyolefins [14]. The different behavior of aromatic units with respect to the aliphatic ones was confirmed by submitting to functionalization under similar conditions a 80/20 by weight mixture of polystyrene with ethylene/1-butene random copolymer. The overall composition of this mixture was analogous to SEBS as far as the aromatic/aliphatic unit ratio and number of branches in the aliphatic blocks are concerned. Analysis of the functionalized product after separation of polystyrene from LLDPE indicated that only the last contained grafted DEM units. The origin of this high selectivity is not clear yet and different stability of benzilic radical versus purely aliphatic [14] radicals and phase segragation can be claimed. As the same molecular and phase features can be maintained in SEBS as in the above homopolymer mixture, one could argue that even SEBS was substantially functionalized in the aliphatic blocks. Accordingly solid-state NMR showed the presence of two new peaks in the single pulse excitation (SPE)-MAS spectra of functionalized SEBS, assigned to the ethyl carbons ($-O-CH_2-CH_3$) of diethyl succinate (DES) formed by DEM insertion [4]. ^{13}C-CP/MAS spectra, which allow signals arising from rigid phases to be enhanced, did not display the above absorptions, thus confirming that the functionalization reaction occurs on the polyolefin blocks. Experiments with SEBS and different polymers to DEM and to DCP ratios showed that FD increases linearly with DEM (Fig. 1) and present a maximum or at least an asymptotic value at a certain DEM/DCP ratio (Fig. 2) as observed in the case of polyolefins [6]. Therefore, considering also the different activation of aromatic and aliphatic units, the same kinetic scheme can be proposed as for LLDPE [5, 6]. (Scheme 1) where DEM propagation is not considered according to previous results [4].

According to Scheme 1 the primary radicals R·formed by thermal decomposition of DCP are likely to be promptly converted according to reactions (2)–(4), in a ratio depending mainly on the relative concentration of the reacting species. Successively, substantially only reaction (5) should occur as indicated by the absence of DEM homo-

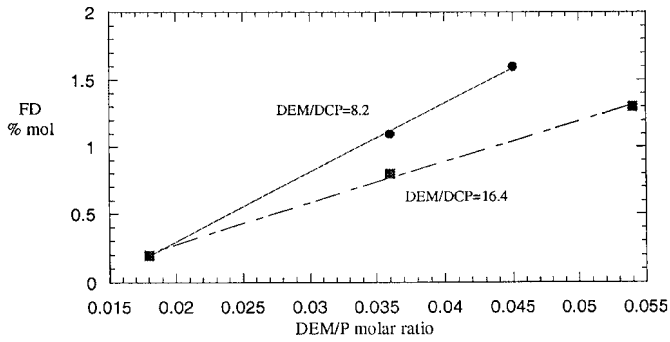


FIGURE 1. Functionalization degree (FD) *v.* monomer (DEM) concentration at two different DEM/free radical initiator (DCP) ratios.

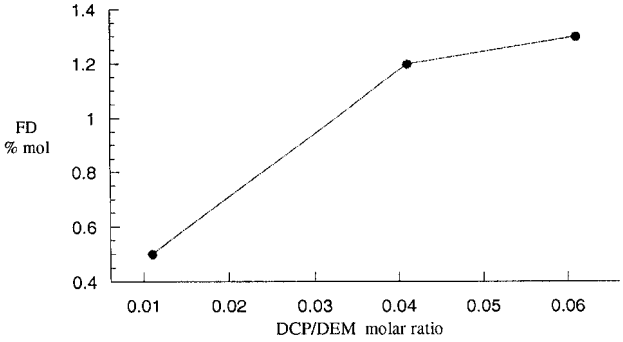


FIGURE 2. Functionalization degree (FD) *v.* free radical initiator/monomer (DCP/DEM) molar ratio.

A) INITIATION

DCP → 2R• (1)

R• + DEM → RDEM• (2)

R• + SEBS → AlSEBS• + RH (3)

R• + SEBS → ArSEBS• + RH (4)

AlSEBS• + DEM → AlSEBSDEM• (5)

B) TRANSFER

RDEM• + SEBS → RDEMH + AlSEBS•(or ArSEBS•) (6)

AlSEBSDEM• + SEBS → AlSEBSDEMH + AlSEBS•(or ArSEBS•) (7)

C) TERMINATION

Al(Ar)SEBS• + Al(Ar)SEBS• → SEBS-SEBS and SEBS + SEBS(-H) (8)

Al(Ar)SEBS• + RDEM• → SEBSDEMR (9)

D) DEGRADATION

2Al(Ar)SEBS• → shorter chain with terminal free radical or double bond (10)

SCHEME 1.

polymer and of DEM grafted on the aromatic units. It is likely that ArSEBS·radicals, because of the high stability, do not react with DEM to produce a radical of lower stability and are rather involved in termination or degradation. The absence of functional groups attached to aromatic units is an indication of the low probability of reaction (9). Indeed RDEM·radicals are probably formed in a very small amount as indicated by the absence of the phenyl group in functionalized ethylene polymers [4]. The resulting effect is a lower efficiency of the initiator with SEBS in respect to a fully aliphatic polymer, which was confirmed by the experimental data (Fig. 3). The occurrence of termination by recombination, and degradation, is in keeping with the broadness of molecular weight distribution (MWD) after the functionalization process and with the presence of aromatic low molecular weight polymer in the acetone soluble fraction. In regards to the functionalization reaction itself, also for SEBS it is based on reaction (5) and it should be linearly dependent on DEM concentration with a lower propagation constant (K_p) due to the lower radical efficiency. On the other side the dependence on DCP concentration cannot be linear but the value must be optimized among the possible reactions (Fig. 2). These data suggest that the free radical functionalization of SEBS can be carried under similar conditions as for polyolefins. The use of an adequate DEM/DCP ratio gives a very acceptable level crosslinking and degradation. Because of the different reactivity of benzil and aliphatic macromolecular radicals the functional groups concentrate in the aliphatic part.

Grafting of Carboxylate Groups onto Styrene/Butadiene Copolymers (SBR)

As mentioned in the introduction, the high number of double bonds in styrene/butadiene copolymers does not allow the direct use of DEM in combination with a free radical initiator. Indeed even with a high excess of DEM the material is rapidly crosslinked in the presence of both DCP or AIBN and the final material could not be used further for elastomer formulation. The crosslinking is the result of the recombination reaction between the allylic free radicals formed through hydrogen abstraction by the primary radicals from the butadiene units. On the other hand crosslinked products can be formed by reaction between macroradicals and double bonds of the butadiene units. In order to hinder this recombination our approach was based on the use of a functionalizing low molecular weight compounds markedly more effective than DEM for the transfer reactions. Thiols are very suitable as they combine a very high transfer capacity of hydrogen to formed radicals with the capacity of the free radical formed on the sulfur atom to add a double bond [16] (Scheme 2).

If R· represents a free radical generated in the SBR macromolecule by a primary free radical formed from an initiator, such as AIBN or DCP, it will be promptly quenched through the transfer reaction with the thiol, and the new radical produced can add to one of the double bonds present in the above macromolecule. The successive transfer with the excess of thiol will end up with converting the butadiene unit into a saturated unit bearing the covalently bonded X group of the thiol. The free radical addition of thiols to olefins proceeds through a rather simple mechanism (Scheme 2) and can be applied to thiols containing a wide number of functional groups. Indeed,

XSH + R• → RH + XS•

XS• + C=C → XS-C-C• $\xrightarrow{+XSH}$ XS-C-CH + XS•

SCHEME 2.

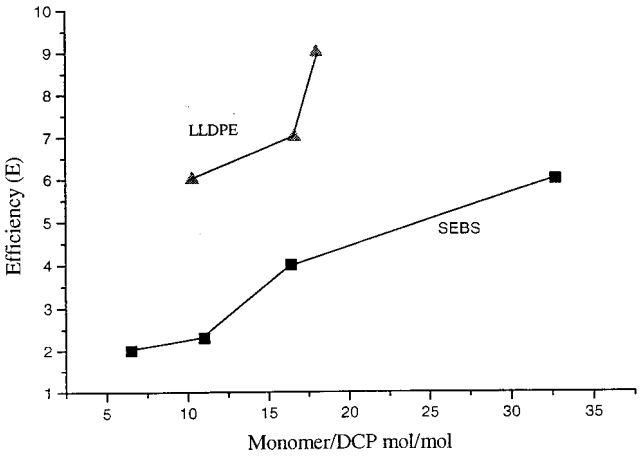


FIGURE 3. Efficiency of (DCP) primary radical in the functionalization of LLDPE and SEBS with diethylmaleate (DEM) at different DEM/DCP ratios.

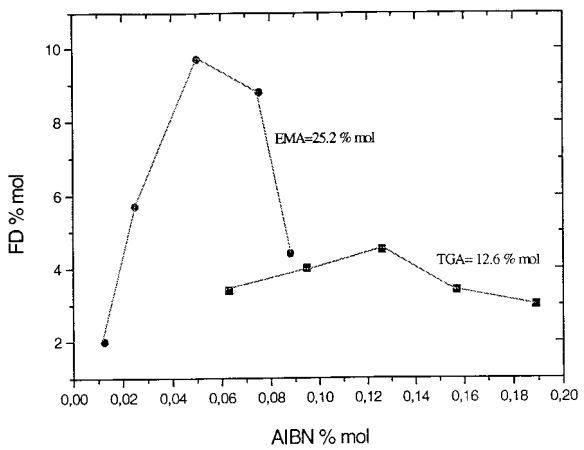


FIGURE 4. Functionalization degree (FD) *v.* radical initiator (AIBN) amount (% mol) in the reactions of SBR with thioglycollic acid (TGA) and ethylmercaptoacetate (EMA).

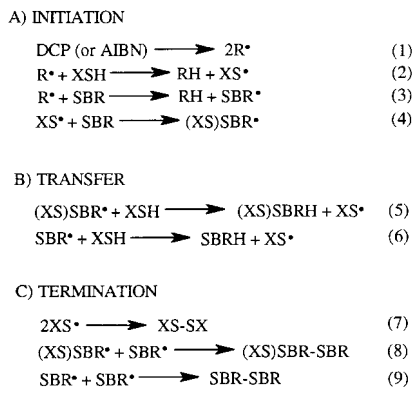
reactions carried out using diazo compounds, peroxides, photosensibilizers (e.g. benzo-phenone) as initiators are widely reported [17–19]. Vinyl double bonds are generally considered as the most reactive and the reactivity decreases with increasing substitution on the double bond; among the 1,2-bisubstituted olefins, the *cis* isomers are more reactive than the *trans* ones. The free radical addition of thiols gives only the "anti-Markovnikov" isomer, owing to the prevalent formation of the more stable radical intermediate. The introduction of thiol derivatives containing carboxylic acid or ester group, into unsaturated aliphatic polymers has been investigated in few paper, and patents [16, 20–21]. Thus the available thioglycollic acid (TGA, $X = CH_2COOH$) or ethylmercaptoacetate (EMA, $X = -CH_2COOC_2H_5$) in the presence of free radical initiators such as AIBN and DCP were comparatively used in our laboratory in order to introduce functional groups into SBR macromolecules [15]. Model studies with terminal and internal low molecular weight olefins indicated unequivocally that the reaction occurs with very high selectivity on the former double bonds. On this basis it was hypothesized that in the case of SBR the reaction is selective towards the vinyl double bonds of the 1,2-butadiene units. This hypothesis was definitively confirmed by ^{1}H-NMR analysis of the functionalized polymer. The FD, expressed as moles of added thiol for one hundred monomeric units of SBR, and the undesirable crosslinking reactions were dependent on the nature of the functional group X on the sulfur atom and the feed composition (Fig. 4). The formation of crosslinked products could be avoided by working at proper XSH/free radical initiator molar ratios. In particular higher FD were obtained in case of EMA whereas TGA was more effective in avoiding crosslinking. Indeed in the presence of AIBN as initiator and under the same temperature and concentration of thiol, EMA gave an FD up to 10 and TGA only up to 5% mol. On the other side, in order to avoid gel formation, an excess of thiol to AIBN larger than 200/1 was necessary for EMA and only larger than 50/1 for TGA. The nature and instantaneous concentration of primary radical also affects both FD and gel formation. With TGA as transfer/functionalizing agent, BPO gives a lower FD and more crosslinking than AIBN under the same conditions.

The glass transition temperature, T_g, of the functionalized SBR increases in an amount depending on FD and nature of the functional groups. The free carboxylic side chains of grafted TGA give a more evident increase probably due to interchain hydrogen bonding. An increase from −47.3 to −28.3 C is observed with 4% mol of TGA, while T_g is still −35 °C with 6–10% mol of EMA. The data obtained allow a qualitative analysis of the reaction mechanism to be made by using a scheme of the involved reactions derived from that previously used (Scheme 1) for the functionalization of saturated polymers with DEM and DCP.

The experimental results about functionalization and gel formation can be discussed with reference to Scheme 3. The functionalization process of reaction (4) is clearly favored by the increased concentration of XSH which participates in producing the functionalizing radical $XS^{\cdot}$ through reactions (2), (5) and (6). These last also inhibit the gel formation by subtracting macromolecular free radicals to the coupling reaction (8) and (9) and crosslinking reaction. The best performances of AIBN with respect to DCP, in term of larger FD and lower gelification, are probably associated with the limited capacity of the primary radicals derived from the former to undergo reaction (3) bearing to undesirable $SBR^{\cdot}$ radicals, while showing the same capacity to reaction (2) giving the effective functionalizing agent $XS^{\cdot}$. Finally reaction (7) is at least partially responsible for the incomplete conversion of the thiol into grafted units and differences between EMA and TGA [15].

CONCLUSION

Limited but controlled amounts of functional



SCHEME 3.

groups can be grafted to the aliphatic monomeric units of styrene/alkene and styrene/diene copolymers through free radical-initiated processes. Undesired degradation and chain extension (including crosslinking) can be reduced and also suppressed by a proper selection of the functionalizing agent and its molar ratio in respect to the free radical initiator. In this way also the functionalization degree can be modulated within limited intervals but to an extent that allow it to maintain the original polymer properties.

Moreover (see Table 1) styrene/butadiene copolymers show different reactivity towards peroxide initiators depending on the double bonds content. We can indeed evaluate the reactivity by measuring the soluble fractions of processed polymers, the total amount of residue being an indirect evidence of high reactivity. It is possible that both styrene copolymers and polyolefins show high reactivity towards the crosslinking reaction depending on unsaturation amount and, among all double bonds, on vinyl unsaturation content. The presence of the styrene phase seems to have no influence on the reactivity thus confirming that macroradicals formed in such a phase may preferentially undergo a transfer reaction rather than addition to the monomer (which leads to a functionalized material) or to double bonds (with the formation of a crosslinked material).

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REFERENCES

1. Cassebras M, Pasqual S, Polton A, Tardi M, Vairon J-P. Synthesis of di- and triblock copolymers of styrene and butyl acrylate by controlled atom transfer radical polymerization. *Macromol. Rapid. Comun.* 1999; **20**:261–264.
2. Pasqual S, Coutin B, Tardi M, Polton A, Vairon J-P. Homogeneous atom transfer polymerization of styrene initiated by 1-chloro-1-phenylethane/copper (I) chloride/bipyridine in the presence of dimethylformamide. *Macromolecules* 1999; **32**:1432–1437.
3. De Roover B, Sclavons M, Carlier V, DeVaux J, Legrad R, Momtaz A. Molecular characterization of maleic anhydride-functionalized polypropylene *J. Polym. Sci., Polym. Chem.* 1995; **33**:829–842.
4. Aglietto M, Bertani R, Ruggeri G, Segre AL. Functionalization of polyolefins. Determination of the structure of functional groups attached to polyethylene by free radical reactions. *Macromolecules* 1990; **23**:1928–1933.
5. Ciardelli F, Aglietto M, Passaglia E, Ruggeri G. Molecular and mechanistic aspects of the functionalization of polyolefins with ester groups. *Macromol. Symp.* 1998; **129**:79–88.
6. Passaglia E, Marrucci M, Ruggeri G, Aglietto M. Chemical reactions affecting the free-radical grafting of diethyl maleate onto ethylene polymers. *Gazzetta Chim. Italiana* 1997; **127**:91–95.
7. Oppolzer W. Intramolecular [4 + 2] and [3 + 2] cycloadditions in organic synthesis. *Angew Chem., Int. Engl. Ed.* 1977; **16**:10–23.
8. Edwards DC, Sato K. Interaction of silica with functionalized SBR. *Rubb. Chem. Technol.* 1980; **53**:66–79.
9. Li T, Topolkaraev VA, Hiltner A, Baer E, JI XZ, Quirk RP. Block copolymers as compatibilizers for blends of linear low density polyethylene and polystyrene. *J. Polym. Sci.: Part B: Polym. Phys.* 1995; **33**:667–683.
10. Matos M, Favis BD, Lomellini P. Interfacial Modification of polymer blends the emulsification curve: 1. Influence of molecular weight and chemical composition of the interfacial modifier. *Polymer* 1995; **36**:3899–3907.
11. Burgisi G, Paternoster M, Peduto N, Saraceno A. Toughness enhancement of polyamide 6 modified with different types of rubber: influence of internal rubber cavitation. *J. Appl. Polym. Sci.* 1997; **66**:777–787.
12. Majumdar B, Paul DR, Oshinski AJ. Evolution of morphology in compatibilized vs uncompatibilized polyamide blends. *Polymer* 1997; **38**:1787–1808.
13. Ciardelli F, Aglietto M, Ruggeri G, Passaglia E, Castelvetro V. Functionalization of polyolefins in the melt through reaction with molecules and macromolecules. *Macromol. Symp.* 1997; **118**:311–316.
14. Passaglia E, Ghetti S, Picchioni F, Ruggeri G. Grafting of diethyl maleate and maleic anhydride onto styrene-b-(ethylene-co-1-butene)-b-styrene triblock copolymer (SEBS). *Polymer*. 2000; **41**:4389–4400.
15. Romani F, Passaglia E, Aglietto M, Ruggeri G. Functionalization of the SBR copolymer by free radical addition of thiols. *Macromol. Chem. Phys.* 1999; **200**:524–530.
16. Sanui K, Lenz RW, MacKnight WJ. Preparation of a polypentenamer having pendant ionic groups and its hydrogenated derivatives. *J. Polym. Sci.* 1974; **12**:1965–1981.
17. Prilezhaeva EN, Shostakovskii NF. Thiolation reactions of ethylene derivatives. *Uspekhi Khim.* 1963; **32**:897–947.
18. Majo FR, Walling C. The peroxide effect in the addition of reagents to unsaturated compounds and in rearrangement reactions. *Chem. Rew.* 1940; **27**:351–412.
19. Ipatieff VM, Pines H, Friedman BS. Reaction of aliphatic olefins with tiophenol. *J. Am. Chem. Soc.* 1938; **60**:2731–2734.
20. Serniuk GE, B. F. Goodrich Co. U.S. Patent n° 2,589,151. 20Thioglycolic acid adducts of rubberlike polymers. *Chem. Abstr.* 1952; 5355e.
21. Brown HP, Standard Oil Developement Co. U.S. Patent no 2,626,248.21Reclaiming polymeric metallocarboxylates. *Chem. Abstr.* 1953; 5160d.

